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REPLY TO ATTN OF:

March 30, 1971

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures contained in the Code GP to Code USI memorandum on this subject, dated June 8, 1970, the attached NASA-owned U.S. patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. :	3,396,057
Corporate Source :	Radio Corporation of America
Supplementary Corporate Source :	
NASA Patent Case No.:	XNP-01959

Please note that this patent covers an invention made by an employee of a NASA contractor. Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the Specification, following the words ". . . with respect to an invention of. . . ."

G Parker

Gayle Parker

Enclosure:
Copy of Patent

Aug. 6, 1968 JAMES E. WEBB 3,396,057

ADMINISTRATOR OF THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

METHOD OF ELECTROLYTICALLY BINDING A LAYER OF SEMICONDUCTORS TOGETHER

Filed Nov. 10, 1964

Fig. 2

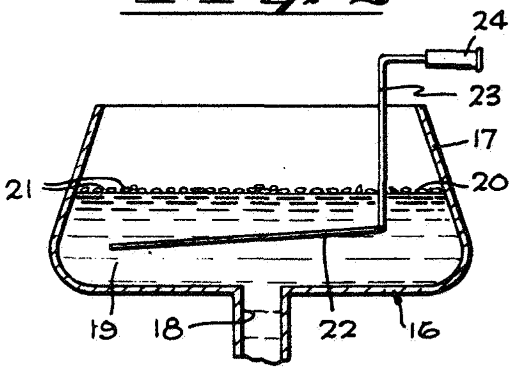

Fig. 3

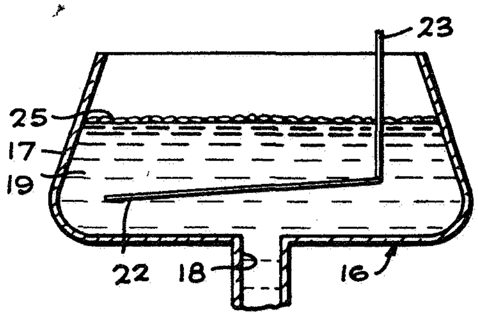

Fig. 4

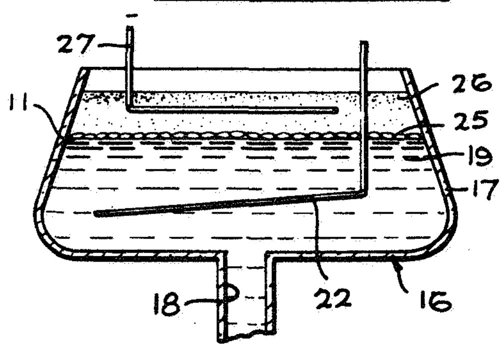

Fig. 5

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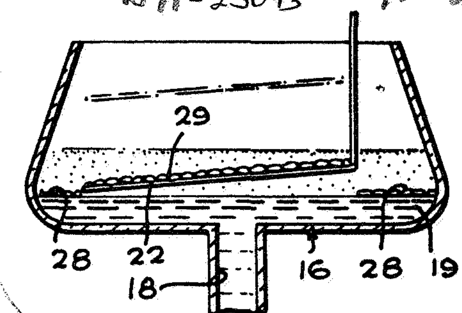
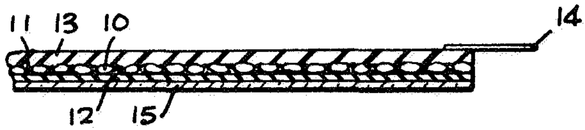


Fig. 1



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United States Patent Office 3,396,057
Patented Aug. 6, 1968

3,396,057
METHOD OF ELECTROLYTICALLY BINDING A LAYER OF SEMICONDUCTORS TOGETHER

James E. Webb, Administrator of the National Aeronautics and Space Administration, with respect to an invention of Sidney G. Ellis, Princeton, N.J.

Filed Nov. 10, 1964, Ser. No. 410,330
7 Claims. (Cl. 136—89)

ABSTRACT OF THE DISCLOSURE

This invention teaches a method of binding a layer of semiconductor particles together. Electro-deposition is used to form an insulating film that holds the particles together. The particles can be used in making solar cells, photoelectric cells and other semiconductor products. Essentially, the particles are deposited on the surface of mercury. The particles float on the mercury. They are compacted and then covered with an electrolyte. One electrode is inserted in the electrolyte while the mercury serves as the other electrode. After the layer is formed, the level of the mercury is lowered so that the now formed layer will adhere to a base member previously submerged in the mercury.

Origin of the invention

This invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85–568 (72 Stat. 435, 42 USC 2457).

Field of the invention

This invention relates to a method of producing a semiconducting product having a single monoparticle layer of semiconductor material and more particularly to a method of providing a single monoparticle layer on a base wherein the particles are bound together by an insulating film so that portions of the particles are exposed to receive subsequent coatings, formations, contacts, etc.

Description of the prior art

In the manufacture of solar cells, selenium cells, photoelectric cells and other semiconductive products, one of the conventional practices has been to coat or apply an amorphous semiconductor material to a metallic base by pressing it cold into the base. For this purpose, the semiconductor material, such as selenium, for example, is made into powder form and is arranged on the base followed by fixing the powder thereto through the application of high mechanical pressure. Subsequently, the fixed powdered base is transformed from its amorphous condition into a crystalline condition. After subjecting the crystalline powdered base to high temperature processing, the powder layer is completely transformed into the metallic condition.

Another practice employed by the prior art involves the floating of semiconductor fluid repellent particles on the surface of a liquid followed by compressing or compacting the particles together to form a continuous layer and subsequently raising a previously submerged base member through the liquid to deposit the particle layer on the base member.

Difficulties have been encountered in practicing these conventional methods because of the time and heating requirements needed for the high mechanical pressure method and the necessity of making the particles liquid repellent in the latter method.

These difficulties are obviated through the employment of the method of the present invention wherein a semiconductor product is provided which does not require the use of liquid repellent particles and which provides an insulating film interconnecting and binding all of the particles of the layer together in such a fashion that opposite polar regions of each particle are exposed for subsequent component attachment or further processing.

Summary of the invention

In general, the method of the present invention provides for the floating of a layer of semiconducting material in powder form on the surface of a fluid having a high density such as metallic liquid represented by mercury, for example. The semiconducting powder is randomly sprinkled on the surface of the mercury and is supported by the mercury. To effect compaction of the particles, the area over which the particles have been sprinkled is caused to be reduced so that a single layer of particles is arranged. The mercury and the particles are covered with a solution compatible with mercury to be used for electro-deposition. A material is electro-deposited to form an insulating film that will hold the particles together about their respective equators. During the electro-deposition portion of the present method, the mercury is electrically conductive and serves as the positive anode. The particle film is deposited on a base previously submerged in the mercury. Therefore, a semiconductor product is provided which includes an insulating matrix deposited electrolytically around the midsections or equatorial planes of the semiconductor particles leaving their polar regions free and exposed for junction, barrier or contact formation.

An object of the present invention is to provide a method of producing a powder coated product whereby the powder forms a uniform single monoparticle layer wherein the particles are insulated from each other.

Another object of the present invention is to provide a method for producing a monoparticle powdered film whereby the particles are, in essence, bound together at their respective centers or midsections leaving the opposite polar regions or ends of the particles exposed and free for other types of contact formations or coatings.

Still a further object is to provide a method for forming a powdered coated product whereby an oxide layer serves to bind the powder together into a monoparticle film as well as to serve as a base for supporting the film.

Another object resides in the feature that the aforementioned fluid serves not only as a support for the powdered particles but the fluid is used as an electrode during the oxidized process.

Brief description of the drawing

The features of the present invention which are believed to be novel are set forth with particularity in the appended claims. The present invention, both as to its organization and manner of operation, together with further objects and advantages thereof, may best be understood by reference to the following description, taken in connection with the accompanying drawings, in which:

FIGURE 1 is a cross-sectional view of a typical product formed by the method of the present invention;

FIGURE 2 is a cross-sectional view of a container for holding mercury having semiconductor material particles supported on its surface as employed in the manufacture of the product of FIGURE 1;

FIGURE 3 is a view similar to that of FIGURE 2 showing compaction of the particles into a layer one particle thick effected through the reduction of mercury surface area by raising its level;

FIGURE 4 is a view similar to FIGURE 3 illustrating the addition of a suitable solution into the container over the compressed particle layer compatible with mercury

for oxidation to form an insulating film holding the particles together; and

FIGURE 5 is a view similar to FIGURE 4 illustrating the depositing of the electro-deposited monoparticle layer onto a supporting screen.

Description of the preferred embodiment

In the practice of this invention, the powder semiconductor material to be coated onto a base member is not required to be naturally liquid repellent or rendered repellent to the liquid carrying media on which the materials are floated in order to prevent the powder materials from sinking in the media. While various liquids may be chosen for supporting the semiconducting material, it is preferable to use a liquid media which is of greater specific gravity than the semiconductor materials so that the materials will float on the surface of the liquid media. A liquid metal such as mercury may be used as a supporting media for the semiconductor materials. Because of the density of mercury, particles of the semiconductor material will not be readily absorbed into the liquid or the liquid absorbed into the particles. Therefore, a feature of the invention resides in employing a fluid media which does not first require treating the particles to prevent them from sinking into the fluid. While a specific metallic fluid medium is given herein for supporting the semiconductor material particles, other well-known high density media, which are intended to be covered herein, will occur to those skilled in the art.

The semiconductor material particles, which need not be either inherently water repellent or artificially liquid repellent, may be placed on the surface of the mercury in any convenient way. The powder may be deposited or scattered so that the particles readily spread over the surface of the liquid. The powder may be applied through a screen or cloth, through an air-blown spray, sprinkling or dusting, or other well-known methods. After depositing the powder on the surface of the mercury, the powdered particles are relatively widely dispersed. In order, therefore, to obtain a continuous coating which is one particle deep or thick, it is necessary to compress the deposited film or coating, or reduce its areas, so that the particles are rearranged relatively close together.

In order to maintain and fix the rearranged particles in close proximity to each other, an insulating film is provided. The film is generated by an oxidation process through electrolysis by introducing a chemical solution compatible with the mercury for causing oxidation to occur. When the liquid is added, it wets the sides and top of the particles but not the bottoms which remain wetted by the supporting mercury. In some cases, depending on the composition of the particles used, it may be necessary to pretreat part of the surface of the particles so the surface will be wetted by the mercury to prevent the solution from getting between the particles and the mercury. A liquid solution that may be used is represented by a soluble tungstate which is employed to cover the compressed particle arrangement on the surface of the mercury. Employing the mercury as a positive anode and applying a negative voltage to the tungstate, oxidation occurs which forms an insulating film at the junction of the tungstate and mercury. This film adheres to the midsection of the particles so that the opposite polar regions extending on the tungstate solution and the mercury respectively remain free and unencumbered by the film.

A clean liquid surface is necessary to insure uniform and constant behavior of the powder on the mercury surface. The powder is deposited on the mercury surface by sifting through a screen, sprinkling, dusting, spraying or by any other convenient method. Just enough powder is deposited to give a dispersed particle arrangement, such as that shown in FIGURE 2. In order to have a continuous, uniform layer or coating of particles one particle thick, it is necessary to compress or concentrate the dispersed particles into a compaction aggregation, such as is shown in FIGURE 3. This may be readily accomplished by the raising of the level of the mercury in the container so that the inwardly disposed sidewalls of the container force the particles into a concentrated arrangement. By raising the level of the mercury, the concentration of powder particles per unit area of mercury surface is increased. If the particle concentration is so increased until incipient cracks or wrinkles begin to form, a continuous coating one particle deep, as shown in FIGURE 3, is attained.

Inasmuch as the particles are of greater density than the tungstate solution, the particles are not absorbed by the solution covering. The electrolytic process is initiated by applying a negative potential to the tungstate solution while a positive potential is applied to the mercury. Oxidation occurs which results in a thin insulating film which binds the particles together into a monoparticle layer. To achieve the fullest effect of the electrolytic process, it may be desirable to prevent the tungstate solution from settling between the particles and the mercury.

A thoroughly cleaned article or base member such as a screen or conducting base member whose upper surface is to be coated, is maintained submerged within the fluid medium beneath the formed insulating film particle layer. After the oxidizing step, the mercury may be withdrawn from the container to lower the formed insulated film particle layer onto the base member. Undersirable extremities of the particle layer will break off from the layer being deposited on the base member as the mercury level continues to be lowered inasmuch as the base member is stationary as it receives the film layer.

For a specific example of the operation of the present method, reference is made to the drawing wherein FIGURE 1 illustrates a typical semi-conductor product manufactured by the method of the present invention. A thin monoparticle layer **10** is shown bound together by an oxide film **11** which is mounted on a base member **12**, such as a screen of fine mesh. It is to be noted that particles are joined by the film about their mid-sections and that the top and bottom of the particles are free of the film so that the bottoms of the particles come into immediate contact and union with the base member. The tops of the particles are covered with a suitable conducting layer **13**. A contact **14** may be fixed to the layer **13** by suitable methods such as evaporation or welding. To complete an electrical product, a suitable conducting barrier **15** may be secured to the side of the base member opposite to its side engaged by the monoparticle layer if the layer **12** does not itself have the appropriate electrical mechanical properties. Other uses and electrical products employing a single monoparticle layer will occur to those skilled in the art.

FIGURE 2 shows a container **16** having an annular inwardly inclined sidewall **17** and a fluid entrance port **18** located in the bottom thereof. Mercury **19** is introduced into the container via port **18** which offers a surface **20** for supporting powdered particles such as represented by particle **21**. A base member **22** is shown submerged in the mercury below the particle scattered surface. The member may be supported by any convenient means; however, a rod **23** having a handle **24** is employed in the illustration for supporting the member as well as for effecting the removal of the member after the particle layer has been deposited thereon. The vertical part of rod **23** should have an insulating coating on it. It is to be noted in this view that the scattered particles are randomly disposed and loosely arranged.

FIGURE 3 illustrates the step of compacting or compressing the loose particle arrangement into a single monoparticle layer by effectively reducing the surface area over which the particles are distributed. This area reduction is achieved by introducing more mercury into the container via port **18** to raise the surface level of the mercury. As the surface level rises, the inwardly inclined sidewall **17** of the container urges the particles together

into a relatively compact single monoparticle layer **25**.

Following the compaction of the particles, FIGURE 4 illustrates the step of depositing an insulating film by introducing a quantity of tungstate solution **26** into the container to cover the monoparticle layer **25**. The weight of the particles prevents the solution from flowing between the particles and the mercury. In some instances, it may be desirable to coat the bottom of the particles with an agent which may be wetted by the mercury to insure against the flow of the solution. The solution may be introduced by any suitable method, but it is suggested that a small pipette be employed for this purpose so that the solution, as it is added, will not disturb the compact particle arrangement.

An electrolytic film **11** is provided by dipping an electrode **27** into the tungstate solution and applying a positive potential to the mercury, using the mercury as an anode. The film interconnects the particles at their equators leaving their opposite polar regions free and exposed for further formation or processing. It is to be noted that FIGURE 4 shows a single compact monoparticle layer bound together by an oxide film.

With reference to FIGURE 5, the single monoparticle layer is shown being deposited onto the base member **22** by removing the mercury from the container via port **18** which lowers the surface level of the mercury. A substantial quantity of mercury is removed so that surface level drops below the previously submerged base member. Preferably, the base member is arranged angularly to the surface level so that the monoparticle layer is progressively deposited thereon as the mercury is removed. It is to be noted that the monoparticle layer extends substantially across the entire length of the mercury surface. However, upon the progressive deposition of the layer onto the mesh **22**, undesired extremities **28** of the layer break away from the main central body **29** portion of the layer which is supported on the mesh.

In the manufacture of other semiconductor products, such as solar cells for example, it is desirable to make ohmic contact to the bottoms of the particles by film **12** and then contact the tops with a transparent conducting layer **13** which would form a photovoltaic barrier with the particles. In this manner, layer **15** is unnecessary.

In the manner described above, the method of the present invention provides a powder coated product as illustrated in FIGURE 1. More specifically, the method provides a container with an inwardly inclined sidewall which is partially filled with mercury. The mercury is fed through the ported bottom portion of the container so as to raise or lower the top surface level of the mercury without disturbance. A semiconducting powder is sprinkled on the mercury surface followed by raising the level of the mercury so that the inclined sidewalls "compact" the particles. Next, the mercury and compacted particles are covered with a tungstate solution to be employed for oxidation. The mercury is, then, covered with an insulating film that will hold the particles together at their midsections. The mercury, being conductive, serves as the positive anode during oxidation. Finally, the mercury level is lowered to deposit the monoparticle film layer onto a mesh or plate previously submerged in the mercury.

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to a preferred embodiment, it will be understood that various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art, without departing from the spirit of the invention; therefore, it is intended that the invention be limited only as indicated by the scope of the following claims.

I claim:

1. A method of manufacturing a powdered semiconductor material product comprising the steps of:
floating powdered semiconducting material on the surface of a liquid having a greater density than that of the material;
electrolytically generating an insulating film at the surface of the liquid in such manner to interconnect said floating powdered semiconducting material together into a single monoparticle layer; and
adhering said generated film layer onto a base member.

2. A method of forming a single monoparticle of semiconductor material comprising the steps of:
floating particles of semiconducting materials in a confined arrangement on the surface of a liquid having a greater density than that of the material;
electrolytically generating an insulating film at the surface of the liquid in such manner to interconnect said floating semiconducting material particles together at their mid-sections into a single monoparticle layer whereby the opposite end regions of the particles are free and exposed; and
adhering said generated film layer onto a base member.

3. A method of producing a monoparticle layer comprising the steps of:
supporting a plurality of particles in a confined random arrangement on a fluid which has a greater density than the particles;
reducing the confined area to compress said supported particles;
electrolytically producing an insulating film at the surface of the liquid joining said compressed particles into a layer in such manner that the film joins the particles about their equators leaving their opposite polar regions free and exposed; and
adhering said oxidized particle layer onto a base member.

4. A method of producing a single monoparticle layer of semiconductor material comprising the steps of:
floating a plurality of semiconductor material particles in a confined random arrangement on an electrically conductive liquid which has a greater density than that of the material;
reducing the confined area to compress said floating particles;
electrolytically producing an insulating film at the surface of said liquid, that joins the particles about their equators leaving their opposite polar regions exposed; and
adhering said particle layer onto a base member so that one surface of said layer remains free and exposed.

5. A method of producing a single monoparticle layer of semiconductor material comprising the steps of:
floating a plurality of semiconductor material particles susceptible to liquid penetration in a confined random arrangement on the surface of a liquid which has a greater density than that of the material;
reducing the area of the particle arrangement to compress said floating particles;
electrolytically producing an insulating film at the surface to the liquid to join said compressed particles into a single layer in such manner that the film joins the particles about their equators leaving their opposite polar regions free and exposed; and
adhering said particle film layer onto a base member previously submerged in the liquid by lowering the liquid level.

6. A method of manufacturing a monoparticle layer wherein each particle is electrically insulated from adjacent particles comprising the steps of:
supporting an arrangement of particles on the surfaces of a liquid metal in a confined area;
reducing the area of said confined particle arrangement to coimpress the particles together;
introducing a solution over said compressed particle arrangement compatible with the liquid metal for effecting oxidation;
passing an electrical current through said solution and metal to form an insulating film that joins said particles into a single monoparticle layer; and

adhering said single monoparticle layer onto a base member.

7. A method of manufacturing a monoparticle layer wherein each particle is electrically insulated from adjacent particles comprising the steps of:

supporting an arrangement of particles on the surface of mercury in a confined area;

reducing the area of said confined particle arrangement to compress the particles together by raising the level-of-mercury;

covering said compressed particle arrangement with a tungstate solution;

passing an electrical current through said mercury and tungstate solution to form an insulating film that holds the particles together at their mid-sections;

adhering said particle film on a mesh previously submerged in the mercury by removing mercury to lower its surface level; and

removing said particle film-bearing mesh from the mercury.

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